

09/743985

PA 148432

PCT / CA 99/00638

29 SEP 1999 (29.09.99)

CA 99/638

REC'D 13 OCT 1999

WIPO PCT

# THE UNITED STATES OF AMERICA

**TO ALL TO WHOM THESE PRESENTS SHALL COME:  
UNITED STATES DEPARTMENT OF COMMERCE**

United States Patent and Trademark Office

CA 99/638

September 09, 1999

**THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM  
THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK  
OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT  
APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A  
FILING DATE UNDER 35 USC 111.**

**APPLICATION NUMBER: 09/116,732**

**FILING DATE: July 16, 1998**

## PRIORITY DOCUMENT

SUBMITTED OR TRANSMITTED IN  
COMPLIANCE WITH RULE 17.1(a) OR (b)



**By Authority of the  
COMMISSIONER OF PATENTS AND TRADEMARKS**

**P. SWAIN**

**Certifying Officer**

carbonates or citrates. These precursors can thus be submitted to various treatments such as evaporation or combustion ( $SS \sim 1-4 \text{ m}^2/\text{g}$ ), to the method of explosion ( $SS < 30 \text{ m}^2/\text{g}$ ), plasma spray-drying ( $SS \sim 10-20 \text{ m}^2/\text{g}$ ) and freeze-drying ( $SS \sim 10-20 \text{ m}^2/\text{g}$ ). However, the drawbacks with all of these methods are that either low specific surface area values are reached or that they are complicated and expensive to put into practice.

The most common method for preparing perovskite catalyst is however the traditional method called "ceramic". This method simply consists in mixing constituent powders (oxides, hydroxides or carbonates) and sintering the powder mixture thus formed to high temperature. The problem with this method is that calcination at high temperature (generally above  $1000^\circ\text{C}$ ) is necessary to obtain the crystalline perovskite structure. Another drawback is that low specific surface area value is obtained ( $SS$  around  $1 \text{ m}^2/\text{g}$ ). An example of such a high temperature heating method is disclosed in U.S. patent No 5,093,301 where a perovskite structure to be used in a catalyst is formed after heating a ground dry powder mixture at  $1300^\circ\text{C}$ .

U.S. patent No 4,134,852 issued in 1979 disclosed a variant to the ceramic method by "mechanically alloying", in the old sense of that expression, the constituent powders necessary for the preparation of perovskite catalyst. Indeed, it refers to a conventional grinding in order to obtain a more or less homogenous mixture of particles but not infer any chemical reaction between the components. It can be read in column 7, lines 5-8 of this patent that "[a] mechanically alloyed powder is one in which precursor components have been intimately intradispersed throughout each particle...". Therefore a necessary step of the process disclosed therein to obtain the desired perovskite structure is by heating the "mechanically alloyed" powder composition to an elevated temperature greater than  $800^\circ\text{C}$  (column 7, lines 61-62).

Today, the use of the expression "mechanical alloying" or "mechanosynthesis" refers among other things to a high energy milling process wherein nanostructural particles of the compounds milled are induced. Therefore it also refers to the production of metastable phases, for example high temperature, high pressure or amorphous phases, from crystalline phases stable under ambient temperature and pressure. For example, the structural transformation of alumina ( $\text{Al}_2\text{O}_3$ ), the

preparation of ceramic oxides and the preparation of stabilized zirconias by high energy milling or mechanical alloying have already been respectively disclosed in the following references: P.A. Zielinski *et al.* in J. Mater. Res., 1993, Vol. 8. pp 2985-2992 ; D. Michel *et al.*, La revue de métallurgie-CIT/Sciences et Génies des matériaux, Feb. 1993; and D. Michel *et al.*, J. Am. Ceram. Soc., 1993, Vol 76, pp 2884-2888. The publication by E. Gaffet *et al.* in Mat. Trans., JIM, 1995, Vol 36, (1995) pp 198-209) gives an overview of the subject.

However, even if these papers disclosed the use of high energy milling, their authors have only been able to transform their starting product from one phase to another phase. The product resulting from the milling thus still has the same structure. Furthermore, none of them disclose the preparation of perovskite.

There is still presently a need for a simple process, low in cost for producing a valuable perovskite. There is also a need for a perovskite-type metal oxide with a high specific surface area and for a process for producing such a perovskite.

#### SUMMARY OF THE INVENTION

An object of the present invention is to propose a process for producing a perovskite-type metal oxide that will satisfy the above-mentioned needs.

According to the present invention, that object is achieved with a process for producing a perovskite of the general formula  $ABO_3$  which comprises the step of subjecting a mixture of starting powders formulated to contain separately the components represented by A and B in the formula to a high energy milling sufficient to induce chemical reaction of the components and thereby synthesize a mechanically-alloyed powder comprising the said perovskite in the form of nanostructural particles.

The component represented by A preferably comprises at least one element selected from the group consisting of La, Sr, Ba, Cr, Rb, Ag, Ca, Pr, Nd, and Bi of the periodic table and the component represented by B preferably comprises at least one element selected from the group consisting of Co, Fe, Ni, Mn, Cr, Ti, Cu, Mg, V, Nb, Ta, Mo and W of the periodic table.

The starting powders are preferably a powder of  $La_2O_3$  and a powder of  $Co_3O_4$ , and in that case, the perovskite is  $LaCoO_3$ .

091157221074598

preparation of ceramic oxides and the preparation of stabilized zirconias by high energy milling or mechanical alloying have already been respectively disclosed in the following references: P.A. Zielinski *et al.* in *J. Mater. Res.*, 1993, Vol. 8, pp 2985-2992 ; D. Michel *et al.*, *La revue de métallurgie-CIT/Sciences et Génies des matériaux*, Feb. 1993; and D. Michel *et al.*, *J. Am. Ceram. Soc.*, 1993, Vol 76, pp 2884-2888. The publication by E. Gaffet *et al.* in *Mat. Trans., JIM*, 1995, Vol 36, (1995) pp 198-209) gives an overview of the subject.

However, even if these papers disclosed the use of high energy milling, their authors have only been able to transform their starting product from one phase to another phase. The product resulting from the milling thus still has the same structure. Furthermore, none of them disclose the preparation of perovskite.

There is still presently a need for a simple process, low in cost for producing a valuable perovskite. There is also a need for a perovskite-type metal oxide with a high specific surface area and for a process for producing such a perovskite.

#### SUMMARY OF THE INVENTION

An object of the present invention is to propose a process for producing a perovskite-type metal oxide that will satisfy the above-mentioned needs.

According to the present invention, that object is achieved with a process for producing a perovskite of the general formula  $ABO_3$ , which comprises the step of subjecting a mixture of starting powders formulated to contain separately the components represented by A and B in the formula to a high energy milling sufficient to induce chemical reaction of the components and thereby synthesize a mechanically-alloyed powder comprising the said perovskite in the form of nanostructural particles.

The component represented by A preferably comprises at least one element selected from the group consisting of La, Sr, Ba, Cr, Rb, Ag, Ca, Pr, Nd, and Bi of the periodic table and the component represented by B preferably comprises at least one element selected from the group consisting of Co, Fe, Ni, Mn, Cr, Ti, Cu, Mg, V, Nb, Ta, Mo and W of the periodic table.

The starting powders are preferably a powder of  $La_2O_3$  and a powder of  $Co_3O_4$  and in that case, the perovskite is  $LaCoO_3$ .

The perovskite obtained may have a BET specific surface area of at least 6 m<sup>2</sup>/g, preferably substantially of 16 m<sup>2</sup>/g.

According to a preferred variant of the invention, the milling step is performed under an atmosphere comprising a gas selected from the group consisting of O<sub>2</sub>, CO<sub>2</sub>, NO<sub>2</sub>, NH<sub>3</sub>, and H<sub>2</sub>S and in that case the BET specific surface area of the perovskite obtained may be at least 20 m<sup>2</sup>/g.

Preferably, the high energy milling is performed in an horizontal shaker mill at an agitation speed of 1000 cycles/min for a period of at least 8 hours.

The present invention also provides a process for producing a perovskite of the general formula ABO<sub>3</sub> having a high BET specific surface area which comprises the steps of:

a) subjecting a mixture of starting powders formulated to contain the components represented by A and B in the formula to a high energy milling sufficient to induce nanostructural particles of the components and thereby synthesize a mechanically-alloyed powder comprising a perovskite; and

b) increasing the BET specific surface area of the perovskite obtained in step a) by further subjecting said perovskite to high energy milling to obtain a perovskite having a high BET specific surface area.

Step b) is preferably performed under a humidified atmosphere or under an atmosphere comprising a gas selected from the group consisting of O<sub>2</sub>, CO<sub>2</sub>, NO<sub>2</sub>, NH<sub>3</sub>, and H<sub>2</sub>S. In the first case, the humidified atmosphere may be obtained by adding a small amount of an aqueous solution to the perovskite obtained in step a) in order to obtain a humidified mechanically-alloyed powder and the perovskite phase obtained following step b) has a BET specific surface area of at least 30 m<sup>2</sup>/g.

In the second case, the milling of step b) is performed under an atmosphere comprising a gas selected from the group consisting of O<sub>2</sub>, CO<sub>2</sub>, NO<sub>2</sub>, NH<sub>3</sub>, and H<sub>2</sub>S and the BET specific surface area of the perovskite is substantially 36 m<sup>2</sup>/g.

As can be appreciated, the process according to the present invention is simple, efficient, not expensive and does not require any heating step for producing a perovskite that may easily show a very high specific surface area. Another advantage is that the perovskite obtained according to the present invention also has a high density of lattice defects thereby showing a higher catalytic activity, a

characteristic which is highly desirable in their eventual application as catalysts and electronic conductors.

A non-restrictive description of preferred embodiments of the present invention will now be given with reference to the appended drawings and tables.

### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is an X-ray diffraction pattern ( $\text{CuK}_\alpha$  wavelength), shown on a scale of  $10^\circ$  to  $80^\circ$  diffraction angle ( $2\theta$ ), of a sample taken after one hour of high energy milling. Peaks corresponding to the starting powders ( $\text{La}_2\text{O}_3$  and  $\text{Co}_3\text{O}_4$ ) and the obtained perovskite ( $\text{LaCoO}_3$ ) can be identified by using the corresponding bars at the bottom of the Figure.

Figure 2 is an X-ray diffraction pattern of a sample taken after four hours of high energy milling.

Figure 3 is an X-ray diffraction pattern of a sample taken after eight hours of high energy milling.

Figure 4 is an X-ray diffraction pattern of a sample taken after sixteen hours of high energy milling. By using the bars at the bottom of the Figure it can be seen that all the major peaks correspond to the produced perovskite  $\text{LaCoO}_3$ .

### DESCRIPTION OF A PREFERRED EMBODIMENT

The present invention relates to a new process called "mechanical alloying" or "mechanosynthesis" for preparing perovskites having the empirical formula  $\text{ABO}_3$  simply by subjecting to high energy milling the components represented by A and B in the formula. The man of the art will understand that A and B are being selected and mixed according to the stoichiometric proportion of the components of the desired perovskite.

As indicated throughout, the term "high energy milling" refers to the condition which is developed in the container of a "high energy mill" and where nanostructural particles of the components in the mill are induced. Examples of such high energy mill include: planetary milling machine (so called G5 and G7), Pulverisette™ (P5 and P7) milling planetary machine, ASI Uni-Ball Mill II™ and SPEX™ horizontal mill.

During the milling, the balls are thus projected violently way and back within the container of the mill. The balls also bang each other within the container. When sufficient mechanical energy is applied to the total charge (balls and powders), it is believed that a substantial portion of the charge is continuously and kinetically maintained in a state of relative motion. To achieve the "mechanosynthesis", the impact energy developed by these repetitive shocks must be sufficient to induce nanostructural particles of the components in the order of 10 to 100 nanometers in order to generate chemico-physical reactions only through mechanical forces.

To illustrate the invention and to give those skilled in the art a better understanding of the invention, the results obtained for the preparation of the perovskite  $\text{LaCoO}_3$  are given below.

Although, in this preferred embodiment, La stands for A and Co stands for B, the range of application of the current process is much larger since, in the empirical formula  $\text{ABO}_3$ , A comprises at least one element selected from the group consisting of La, Sr, Ba, Cr, Rb, Ag, Ca, Pr, Nd, and Bi of the periodic table and B comprises at least one element selected from the group consisting of Co, Fe, Ni, Mn, Cr, Ti, Cu, Mg, V, Nb, Ta, Mo and W of the periodic table.

Thereby, according to the process of the invention, perovskite of the formula  $\text{A}_{1-x}\text{A}'_x\text{B}_{1-y}\text{B}'_y\text{O}_3$ , where A and A' are of the same valence and B the same valence as B', could be prepared. Accordingly, multiple oxides (triple, quadruple, etc...) such as  $\text{La}_x\text{Sr}_{1-x}\text{CoO}_3$ ,  $\text{La}_x\text{Sr}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_3$  and  $\text{La}_{x1}\text{Sr}_{x2}\text{Ba}_{1-x1-x2}\text{Co}_{y1}\text{Fe}_{y2}\text{Ni}_{1-y1-y2}\text{O}_3$  could also be produced just by selecting and mixing the starting powders according to the stoichiometric proportion constituting the desired perovskite. Among these potential products, the ones having the most important commercial values are  $\text{LaCoO}_3$ ,  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.85}\text{Fe}_{0.15}\text{O}_3$ , and  $\text{NdMnO}_3$ .

To form the perovskite the starting materials are selected on a basis of availability and cost provided that the form is suitable (i.e. fine powder) and unwanted additives are not introduced into the product. In the following preferred embodiments of the invention, lanthanum has been introduced as the elementary oxide  $\text{La}_2\text{O}_3$  and cobalt as the elementary oxide  $\text{Co}_3\text{O}_4$ . Compounds such as hydroxides, carbonates, nitrates, oxalates, chlorates could also be used.

**EXAMPLE I**

In normal milling conditions, starting powders are weighed and mixed in the desired proportion leading to the composition of the final compound. In this specific example, 3.3 g of lanthanum oxide ( $\text{La}_2\text{O}_3$ ) and 1.7 g of cobalt oxide ( $\text{Co}_3\text{O}_4$ ) were introduced in a cylindrical tempered steel container having 5 mm thick wall with three tempered steel balls [two of 7/16 inches diameter (11 mm) and one of 9/16 inches diameter (14 mm)]. Preferably, the total powder weight inserted into the container is about 5 to 7 g. The container is closed with a thick cover and hermetically sealed with a Viton™ O-ring. To vary the energy of milling impacts, different sets of balls having various sizes and specific densities may be used.

The container is inserted horizontally in a laboratory SPEX™ shaker mill and the milling normally proceeds at an agitation speed of 1000 cycles per minute for a period varying from 1 to 20 hours.

Although the milling proceeds at room temperature, the numerous balls shocks within the container increase its temperature. Thus the container was fan cooled and its temperature was thus kept below 40°C. Sampling were also performed at 1, 4, 8, 16 and 20 hours of milling and the crystalline structure of the product was determined by X-ray diffractometry using a Philips or a Siemens D5000™ diffractometer. In both cases, the  $\text{CuK}_\alpha$  was used ( $\lambda = 1.54$  Angstrom). Spectra were recorded in a step scanning from 10 to 80° in 2θ angle with a 2.4 s for each 0.05° step. Correct identification of the compounds was performed by comparing the patterns obtained with the patterns found in a patterns' library.

The specific surface area of the product was determined by using the Brunauer, Emmet, and Teller method (BET) using a computer-controlled sorption analyzer (Omnisorb 100™) from Omicron, operating in continuous mode. Samples of about 1 g were heated under a vacuum at various temperatures (see Table 1) until complete removal of humidity (20 to 24 hours) prior to the adsorption-desorption experiments. Nitrogen adsorption measurement was performed at liquid nitrogen temperature, with a scanning pressure of up to 75 Torr.

Figures 1 to 4 illustrate the X-ray patterns allowing to deduct the evolution of the crystalline structure from the product found in the container at different period during the milling.



As seen in Figure 1, after one hour of milling, the typical patterns of the two starting oxides  $\text{La}_2\text{O}_3$  and  $\text{Co}_3\text{O}_4$  are clearly seen. Perovskite-type structure ( $\text{LaCoO}_3$ ) begins to stand out.

As shown in Figures 2 and 3 after four and eight hours of milling, the intensities of the starting oxides peaks diminish gradually. It can also be appreciated that the peaks of the perovskite-type structure grow accordingly.

After sixteen hours of milling (Figure 4), the content of the container is practically all converted in perovskite since the patterns of the two starting oxides have almost all disappeared. The major peaks thus show exclusively the presence of perovskite structure compound. In fact, this X-ray pattern shows that about 95% of the content of the powder within container consists of perovskite after sixteen hours of milling. Specific surface area measurements revealed that this final compound has a specific surface area of about  $16 \text{ m}^2/\text{g}$ , a value distinctly higher than that of conventional method which is only in the order of a few  $\text{m}^2/\text{g}$ .

It has also been discovered that the milling performance may be increased by replacing the normal milling atmosphere. For example, in a second variant of the process, the milling atmosphere was replaced by injecting into the container pure oxygen ( $\text{O}_2$ ). This causes the speed of the reaction to be slightly increased. The complete conversion (as evaluated by X-ray diffraction) of the starting oxides to perovskite was obtained in 14 hours as compared to 16 hours where the atmosphere was not changed.

Likewise, it is believed that the use of other gases such as  $\text{CO}_2$ ,  $\text{NO}_2$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{S}$ , instead of using ambient air as the reaction atmosphere, may have a positive effect on the milling reaction. More particularly, it increases the speed of the reaction and/or it increases the specific surface area of the resulting perovskite.

Since the milling is normally performed in a steel container, iron contamination in the final compound was measured. Analysis showed that following 20 hours of normal milling, this contamination is minor since it constitutes less than 1% of the final compound as detected by scanning electronic microscopy (data not shown).

In order to improve the specific surface area of the perovskite obtained in normal milling conditions, various milling conditions were tested. These include: replacing the tempered steel balls and container by tungsten one's; increasing the

duration of milling; and submitting the perovskite obtained after normal milling conditions to a subsequent milling step, called a post-treatment, under a modified atmosphere.

## EXAMPLE II

It is believed that during the high energy milling using a sealed container, the oxygen contained in the trapped air is rapidly consumed by the metallic atoms exposed to the surface newly created by the breaking of crystals under the repetitive impacts within the container. Thus, very rapidly, the milling is performed under an inert nitrogen atmosphere. In such conditions, the exposed surfaces "stick back" together, giving perovskite with lower specific surface area. Therefore, like for the first step, the Applicant modified the normal milling atmosphere in order to increase the specific surface area.

For example, in a third preferred embodiment, perovskite was first synthesized in a sealed container according to example 1. Then the perovskite newly synthesized was further high energy milled for a period of up to 72 hours under constant level oxygen atmosphere. Oxygen level was kept to a normal level (air) by replacing the sealed joint of the container by a filter-paper ring in order to let the normal air to seep into the container. By doing so, the BET specific surface area of the milled perovskite was increased from about 16 m<sup>2</sup>/g to about 23 m<sup>2</sup>/g.

Likewise, it is believed that the use of other reactive gases such as CO<sub>2</sub>, NO<sub>2</sub>, NH<sub>3</sub>, and H<sub>2</sub>S, instead of using ambient air as the reaction atmosphere, may have a positive effect on the milling reaction (increase of the speed of the reaction and/or increase of the specific surface area of the resulting perovskite, etc.).

## EXAMPLE III

In a fourth variant, the perovskite was obtained after normal milling conditions in a tungsten carbide container. However, since the density of the tungsten carbide balls is higher than the one of tempered steel balls, the speed of agitation must be reduced to avoid the destruction of the container or the balls.

In a fifth variant, the perovskite obtained in normal milling conditions was post-treated. This post-treatment comprises further high energy milling of the perovskite

under an humidified atmosphere. Preferably, to obtain said humidified atmosphere, a small quantity of water (six drops) was simply added to said perovskite (~5 g), the container was sealed and the whole was submitted to a subsequent normal milling for one to six hours.

5 Table 1 presents the specific surface area measurements using the BET method following the milling of lanthanum oxide ( $\text{La}_2\text{O}_3$ ) and cobalt oxide ( $\text{Co}_3\text{O}_4$ ) in order to obtain a perovskite structure of the type  $\text{LaCoO}_3$  according to the first, fourth or fifth preferred embodiment of the invention.

As can be appreciated, the milling within a tungsten carbide container (samples 1 and 2) does not improve the specific surface area of the resulting perovskite as compared to perovskite obtained within a tempered steel container (example I, sample 3). However, further high energy milling of the perovskite under a humidified atmosphere provides a perovskite having a specific surface area of up to about  $36 \text{ m}^2/\text{g}$  (sample 4), one of the highest value reached in the art. The humidified milling atmosphere created by the addition of water during the subsequent milling of the perovskite is thus one of the factors which have an important positive influence on the increase of the specific surface area of the perovskite obtained according to this process.

20 The catalytic activity of the post-treated perovskite (sample 4) was also evaluated and compared with the catalytic activity of sample 1. As seen in Table 2, the perovskite obtained following the post-treatment has a Minimal Temperature of Total Conversion (MTTC) lower than the untreated perovskite. It has been calculated that this  $70^\circ\text{C}$  difference to the advantage of the post-treated sample, corresponds to a catalytic activity superior by a factor of about 600 to 2000 times over sample 1. 25 Such an increase is largely superior (from about 50 to 200 times) to what should have been normally obtained for a perovskite having a specific surface area of  $36 \text{ m}^2/\text{g}$ , since the specific surface area ratio of the post-treated perovskite (sample 4) over the untreated (sample 1) is only 11.6 ( $36/3.1$ ).

30 These results thus show that, besides having a high specific surface area, the post-treated perovskite obtained according to this variant of the process of the invention also has a high density of lattice defects thereby having a higher catalytic activity. A high density of lattice defects is a characteristic which is highly desirable

for the eventual application of the perovskite as catalyst and in electronic conductive components.

According to another aspect of the invention, the perovskite may be doped with a transition group metal or a precious group metal. In the industry, the doping of a perovskite used as catalyst enables the sulfur poisoning (SO<sub>2</sub>) to be reduced. Preferably the doping metal used for doping the perovskite is selected from the group consisting of platinum, ruthenium, rhodium, nickel, cobalt, iron and copper.

The doping is preferably performed only once the perovskite has been synthesized since an early doping would reduce the specific surface area of the synthesized perovskite. Advantageously, the doping can be performed during the post-treatment step with the help of a piece of the selected doping metal inserted in the container during the subsequent high energy milling. However, the perovskite obtained after the milling could also be doped by treating said perovskite with a deposit of the doping metal.

Although preferred variants of the invention according to the present invention have been described in detail herein and illustrated in the accompanying figures and tables, it is to be understood that the invention is not limited to these precise embodiments and that various changes and modifications may be effected therein without departing from the scope or spirit of the invention.

For example, a planetary ball-milling machine could be used instead of an horizontal mill. Starting powders could also be grinded before their high energy milling. Likewise, the perovskite obtained after the milling according to the process of the invention, could also be treated to increase its catalytic activity by removing its iron contamination.

**TABLE I****Specific surface area measurements using the BET method**

Sample	Milling conditions and duration	Surface area measurements (BET)	
		Heating temperature (°C)	Surface area (m <sup>2</sup> /g)
1	A) Normal milling: Duration = 12 hours Atmosphere = air Container + Balls = Tungsten carbide Speed = 700 cycles/min	400	3.1
2	A) Normal milling: Duration = 20 hours Atmosphere = air Container + Balls = Tungsten carbide Speed = 700 cycles/min	200 400	5.6 7.6
3	A) Normal milling: Duration = 20 hours Atmosphere = air Container + Balls = Tempered steel Speed = 1000 cycles/min	200 380	10.2 16.3
4	A) Normal milling: Duration = 24 hours Atmosphere = air Container + Balls = Tempered steel Speed = 1000 cycles/min  B) Post-treatment: Duration: = Subsequent milling for 6 hours Atmosphere = Humidified Container + Balls = Tempered steel Speed = 1000 cycles/min	200 370	35.9 32.1

**TABLE II**

**Comparison of the catalytic activity\* of standard perovskite with the post-treated perovskite obtained according to the method of the invention**

Perovskite	Specific surface area (m <sup>2</sup> /g)	MTTC**
Untreated (sample 1)	3.1	295°C
Post-treated (sample 4)	36	225°C

\* Measured by the conversion of n-Hexane  
(Conditions:  $y_{C_6H_{14}} = 1\%$ ;  $y_{O_2} = 89.1\%$ ; Catalyst weight =  $0.105 \pm 0.0015$  g)

\*\* MTTC = Minimal Temperature of Total Conversion at a space velocity of  $22\,500\text{ h}^{-1}$ .

**WHAT IS CLAIMED IS:**

1. A process for producing a perovskite of the general formula  $ABO_3$  which comprises the step of subjecting a mixture of starting powders formulated to contain separately the components represented by A and B in the formula to a high energy milling sufficient to induce chemical reaction of the components and thereby synthesize a mechanically-alloyed powder comprising said perovskite in the form of nanostructural particles.
2. A process according to claim 1, wherein:  
A comprises at least one element selected from the group consisting of La, Sr, Ba, Cr, Rb, Ag, Ca, Pr, Nd, and Bi of the periodic table; and  
B comprises at least one element selected from the group consisting of Co, Fe, Ni, Mn, Cr, Ti, Cu, Mg, V, Nb, Ta, Mo and W of the periodic table.
3. A process according to claim 2, wherein the starting powders are a powder of  $La_2O_3$  and a powder of  $Co_3O_4$ .
4. A process according to claim 3, wherein the perovskite is  $LaCoO_3$ .
5. A process according to claim 4, wherein the perovskite has a BET specific surface area of at least  $6 \text{ m}^2/\text{g}$ .
6. A process according to claim 5, wherein the BET specific surface area of the perovskite is substantially  $16 \text{ m}^2/\text{g}$ .
7. A process according to claim 1, wherein the milling step is performed under an atmosphere comprising a gas selected from the group consisting of  $O_2$ ,  $CO_2$ ,  $NO_2$ ,  $NH_3$ , and  $H_2S$  and wherein the BET specific surface area of the perovskite obtained is at least  $20 \text{ m}^2/\text{g}$ .
8. A process according to claim 7, wherein the BET specific surface area of the perovskite obtained is substantially  $23 \text{ m}^2/\text{g}$ .

9. A process according to claim 1, wherein the high energy milling is performed in an horizontal shaker mill at an agitation speed of 1000 cycles/min for a period of at least 8 hours.

5 10. A process for producing a perovskite of the general formula  $ABO_3$  having a high BET specific surface area which comprises the steps of:

a) subjecting a mixture of starting powders formulated to contain the components represented by A and B in the formula to a high energy milling sufficient to induce nanostructural particles of the components and thereby synthesize a mechanically-alloyed powder comprising a perovskite;

b) increasing the BET specific surface area of the perovskite obtained in step a) by further subjecting said perovskite to high energy milling to obtain a perovskite having a high BET specific surface area.

10 15 11. A process according to claim 10, wherein the high energy milling of step b) is performed under a humidified atmosphere.

12. A process according to claim 11, wherein the humidified atmosphere is obtained by adding a small amount of an aqueous solution to the perovskite obtained in step a) in order to obtain a humidified mechanically-alloyed powder.

20 13. A process according to claim 12, wherein the perovskite phase obtained following step b) has a BET specific surface area of at least  $30 \text{ m}^2/\text{g}$ .

25 14. A process according to claim 10 wherein the high energy milling of step b) is performed under an atmosphere comprising a gas selected from the group consisting of  $O_2$ ,  $CO_2$ ,  $NO_2$ ,  $NH_3$ , and  $H_2S$ .

30 15. A process according to claim 13, wherein the BET specific surface area of the perovskite is substantially  $36 \text{ m}^2/\text{g}$ .

16. A perovskite obtained according to the process defined in claim 1.



17. A perovskite obtained according to the process defined in claim 7.
18. A perovskite having a BET specific surface area of at least 30 m<sup>2</sup>/g .
19. A perovskite having a BET specific surface area of 36 m<sup>2</sup>/g.

**ABSTRACT**

Perovskite-type structure compounds having the general empirical formula  $ABO_3$  are prepared by a process comprising subjecting a mixture of starting powders formulated to contain the components represented by A and B in the formula to a high energy milling sufficient to induce chemical reaction of the components and thereby synthesize a mechanically-alloyed powder comprising the perovskite in the form of nanostructural particles. The process according to the present invention is simple, efficient, not expensive and does not require any heating step for producing a perovskite that may easily show a very high specific surface area. Another advantage is that the perovskite obtained according to the present invention also has a high density of lattice defects thereby showing a higher catalytic activity, a characteristic which is highly desirable in their eventual application as catalysts and electronic conductors.

5

1001672-03468

### DECLARATION FOR PATENT APPLICATION

As a below named inventor, I (we) hereby declare that my (our) residence, post office address and citizenship are as stated below next to my (our) name; I (we) believe that I am (we are) the original, first and sole inventor(s) (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention (Design, if applicable) entitled:

A PROCESS FOR SYNTHESIZING PEROVSKITES

the specification of which (check one): X is attached hereto; \_\_\_\_\_ was filed on \_\_\_\_\_ as application serial No. \_\_\_\_\_ and was amended on (or amended through) \_\_\_\_\_ (if applicable); was filed on \_\_\_\_\_ as International Application (PCT) No. \_\_\_\_\_ and amended on \_\_\_\_\_ (if applicable). I (we) hereby state that I (we) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment(s) referred to above. I (we) acknowledge the duty to disclose information known by me (us) to be material to the patentability of my (our) invention in accordance with Title 37, Code of Federal Regulations, § 1.56(a). I (we) hereby claim foreign priority benefits under Title 35, United States Code § 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application which priority is claimed.

I (We) hereby claim foreign priority benefits under Title 35, United States Code § 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application which priority is claimed.

Prior Foreign Application(s)

Priority Claimed

(Number) (Country) (Day/Month/Year Filed)

YES NO

(Number) (Country) (Day/Month/Year Filed)

YES NO

I (we) hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code § 112, I (we) acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, § 1.56 which occurred between the filing date of the prior art application and the national or PCT international filing date of this application:

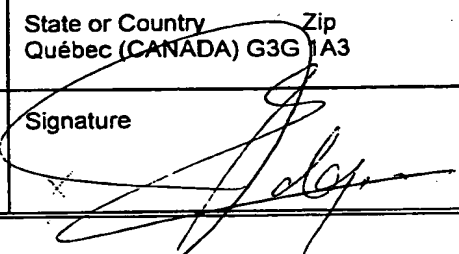
Appl. No.) (Filing date) (Status-Patented, Pending or Aband.)

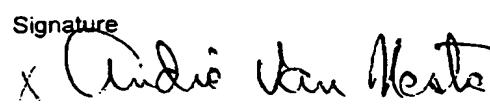
(Appl. No.) (Filing date) (Status-Patented, Pending or Aband.)

I (we) hereby declare that all statements made herein of my (our) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

**POWER OF ATTORNEY:** I (we) hereby appoint as my (our) attorneys, with full powers of substitution and revocation, to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

Garabed NAHABEDIAN (reg. No. 29,507); Thierry ORLHAC (reg. No. 29,497); Alain PROVOST (reg. No. 33,143); Nicolas PELLEMANS (reg. No. 38,797); and Nathalie JODOIN (reg. No. 41,558) whose professional address is 55 St Jacques, Montreal, Quebec, Canada, H2Y 3X2.

Full name of First Inventor Serge KALIAGUINE	Citizenship Canadian
Residence Address-Street 2152 rue Légaré	Post Office Address-Street 2152 rue Légaré
City Lac Saint-Charles	City Lac Saint-Charles
State or Country      Zip Québec (CANADA) G3G 1A3	State or Country      Zip Québec (CANADA) G3G 1A3
Date X      30.06.98	Signature 

Full name of Second Inventor André VAN NESTE	Citizenship Canadian
Residence Address-Street 1127 avenue Beaupré	Post Office Address-Street 1127 avenue Beaupré
City Sainte-Foy	City Sainte-Foy
State or Country      Zip Québec (CANADA) G1W 4B6	State or Country      Zip Québec (CANADA) G1W 4B6
Date X      30.06.98	Signature X 

0011622-01699

Applicant or Patentee: UNIVERSITÉ LAVAL

Serial or Patent No.: \_\_\_\_\_

Attorney's docket No.: \_\_\_\_\_

Filed or Issued: \_\_\_\_\_

For: A PROCESS FOR SYNTHESIZING PEROVSKITES

VERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY STATUS  
(37 CFR 1.9(f) and 1.27(b)) - NONPROFIT ORGANIZATION

I hereby declare that I am an official empowered to act on behalf of the nonprofit organization identified below:

NAME OF ORGANIZATION UNIVERSITÉ LAVAL

ADDRESS Cité Universitaire, Québec (Québec) CANADA G1K 7P4

TYPE OF ORGANIZATION

- (X) UNIVERSITY OR OTHER INSTITUTION OF HIGHER EDUCATION  
( ) TAX EXEMPT UNDER INTERNAL REVENUE SERVICE CODE (26 USC 501(a) and 501(c) (3))  
( ) NONPROFIT SCIENTIFIC OR EDUCATIONAL UNDER STATUTE OF STATE OF THE UNITED STATES OF AMERICA  
(Name of State \_\_\_\_\_ Statute \_\_\_\_\_)  
( ) WOULD QUALIFY AS TAX EXEMPT UNDER INTERNAL REVENUE SERVICE CODE (26 USC 501(a) and 501(c)(3)) IF  
LOCATED IN THE UNITED STATES OF AMERICA  
( ) WOULD QUALIFY AS NONPROFIT SCIENTIFIC OR EDUCATIONAL UNDER STATUTE OF STATE OF THE UNITED  
STATES OF AMERICA IF LOCATED IN THE UNITED STATES OF AMERICA  
(Name of State \_\_\_\_\_ Statute \_\_\_\_\_)

I hereby declare that the nonprofit organization identified above qualifies as a nonprofit organization as defined in 37 C.F.R. 1.9(e) for purposes of paying reduced fees under section 41(a) or (b) of Title 35, United States Code with regard to the invention entitled:

A PROCESS FOR SYNTHESIZING PEROVSKITES

by inventor(s): Serge KALIAGUINE and André VAN NESTE  
described in:

(X) the specification filed herewith

( ) application serial No. \_\_\_\_\_, filed \_\_\_\_\_

( ) patent No. \_\_\_\_\_, issued \_\_\_\_\_

I hereby declare that rights under contract or law have been conveyed to and remain with the nonprofit organization with regard to the above-identified invention.

If the rights held by the nonprofit organization are not exclusive, each individual, concern or organization having rights to the invention is listed below\* and no rights to the invention are held by any person, other than the inventor, who could not qualify as a small business concern under 37 C.F.R. 1.9(d) or by any concern which would not qualify as a small business concern under 37 C.F.R. 1.9(d) or a nonprofit organization under 37 C.F.R. 1.9(e).

FULL NAME \_\_\_\_\_

ADDRESS \_\_\_\_\_

( ) INDIVIDUAL ( ) SMALL BUSINESS CONCERN ( ) NONPROFIT ORGANIZATION

FULL NAME \_\_\_\_\_

ADDRESS \_\_\_\_\_

( ) INDIVIDUAL ( ) SMALL BUSINESS CONCERN ( ) NONPROFIT ORGANIZATION

( ) See attached sheet for additional person(s), concern(s), or organization(s)

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28(b)).

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

NAME OF PERSON SIGNING: X

LOUISE FILION  
VICE-RECTRICE À LA RECHERCHE

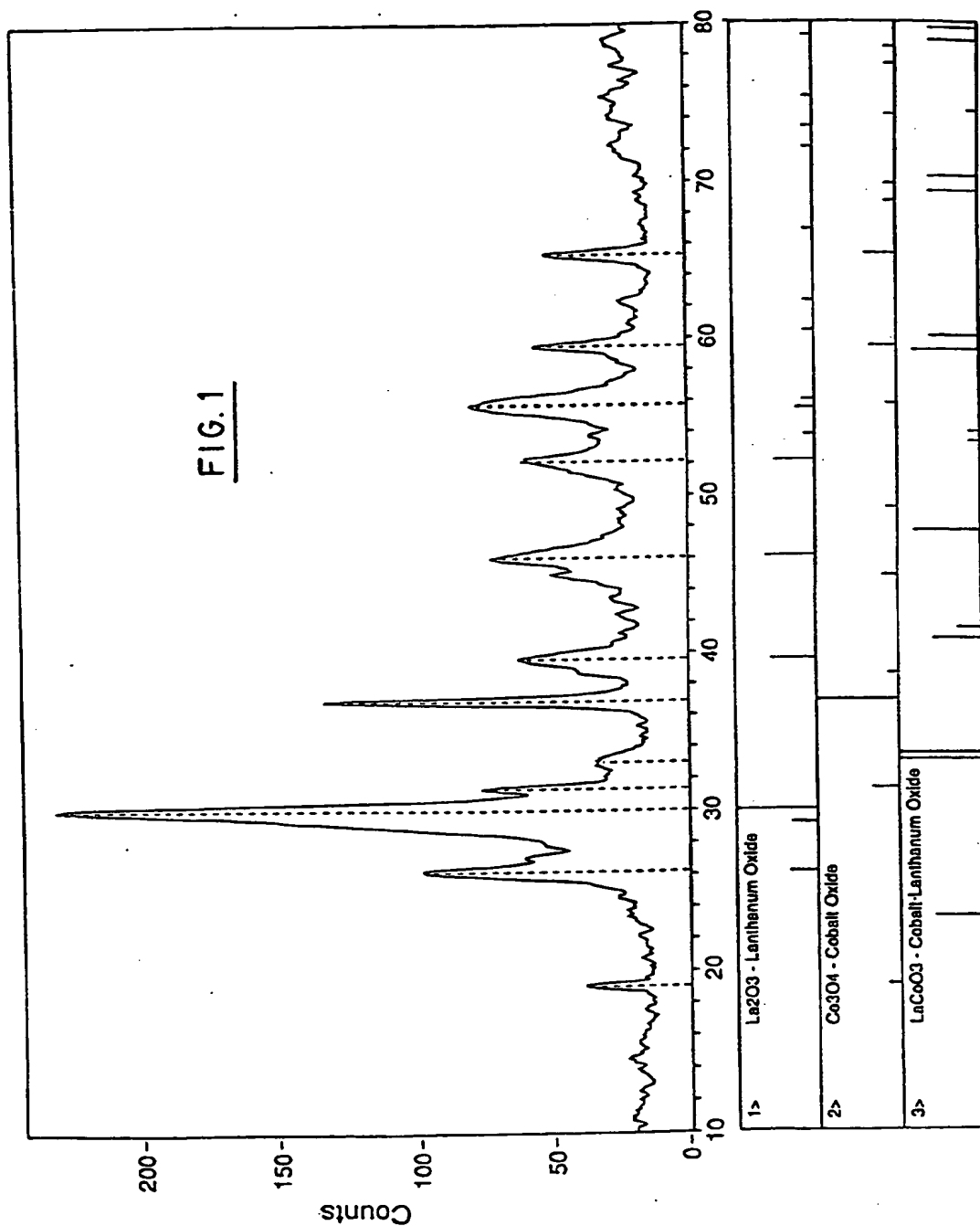
TITLE OF PERSON OTHER THAN OWNER X

ADDRESS OF PERSON SIGNING: Sciences of Education Building, room 2554, UNIVERSITE LAVAL  
Ste-Foy, Qc, Cda G1K 7P4

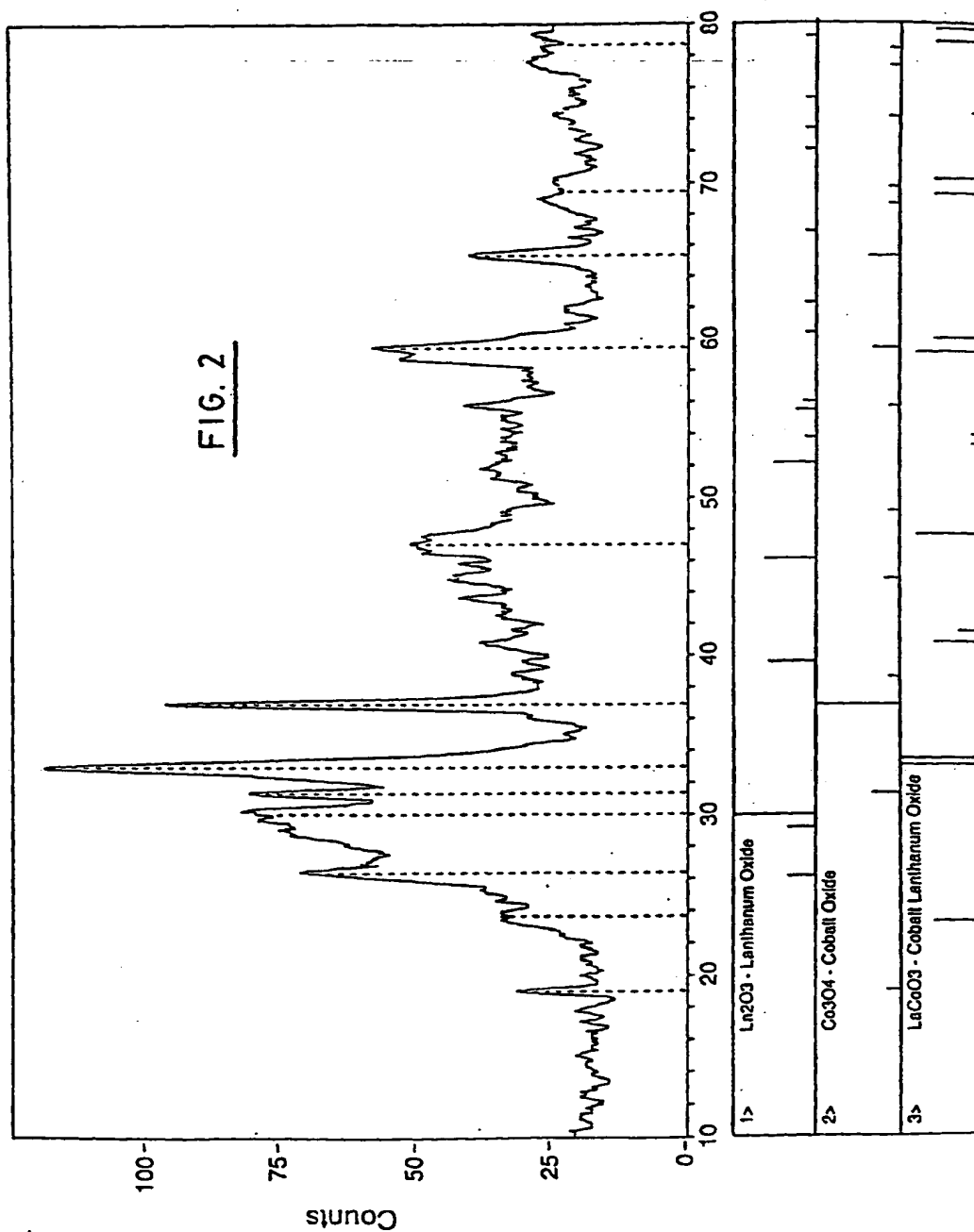
SIGNATURE: X

DATE: July 3, 1998

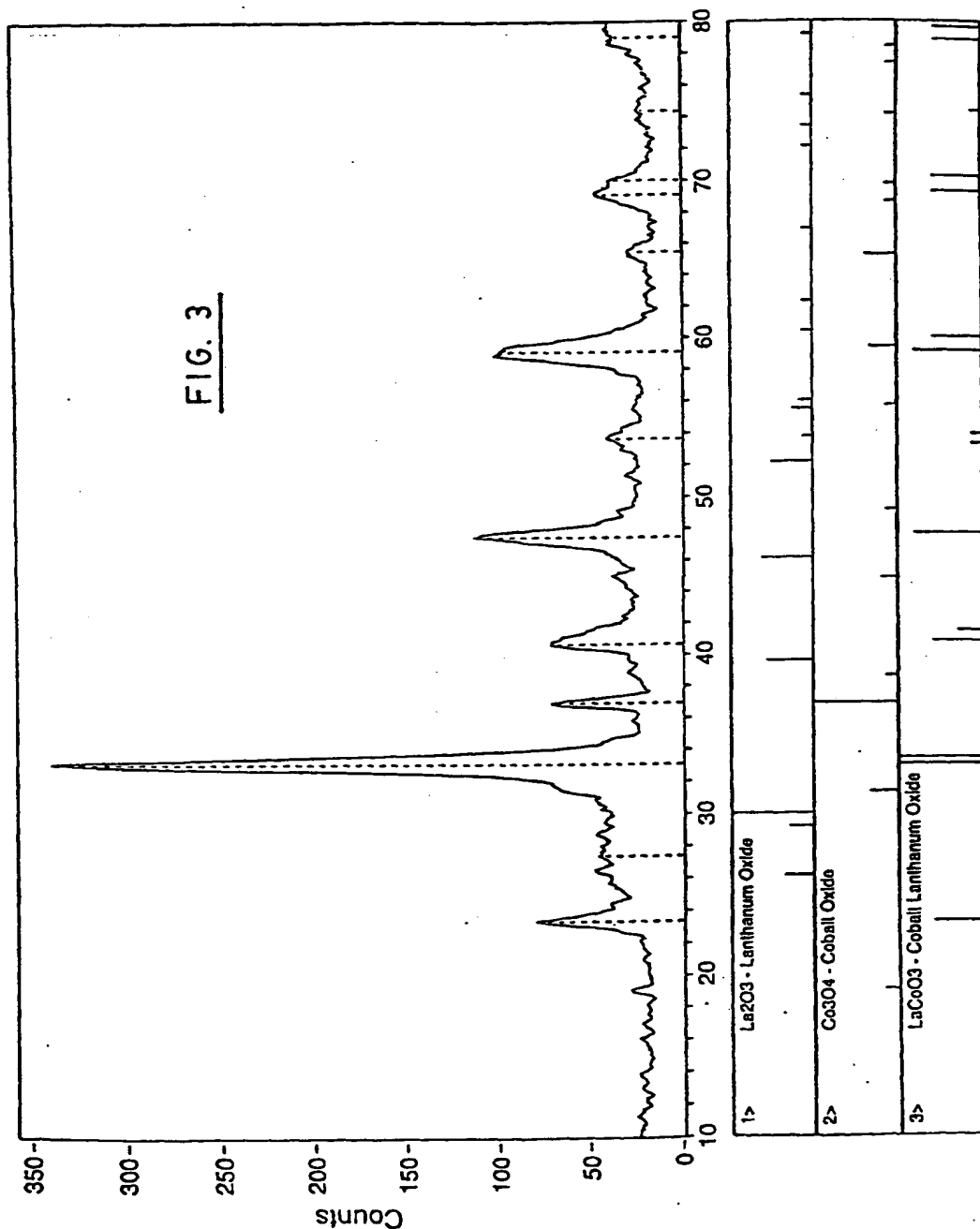
869T40-2E29T60



869740-2269760

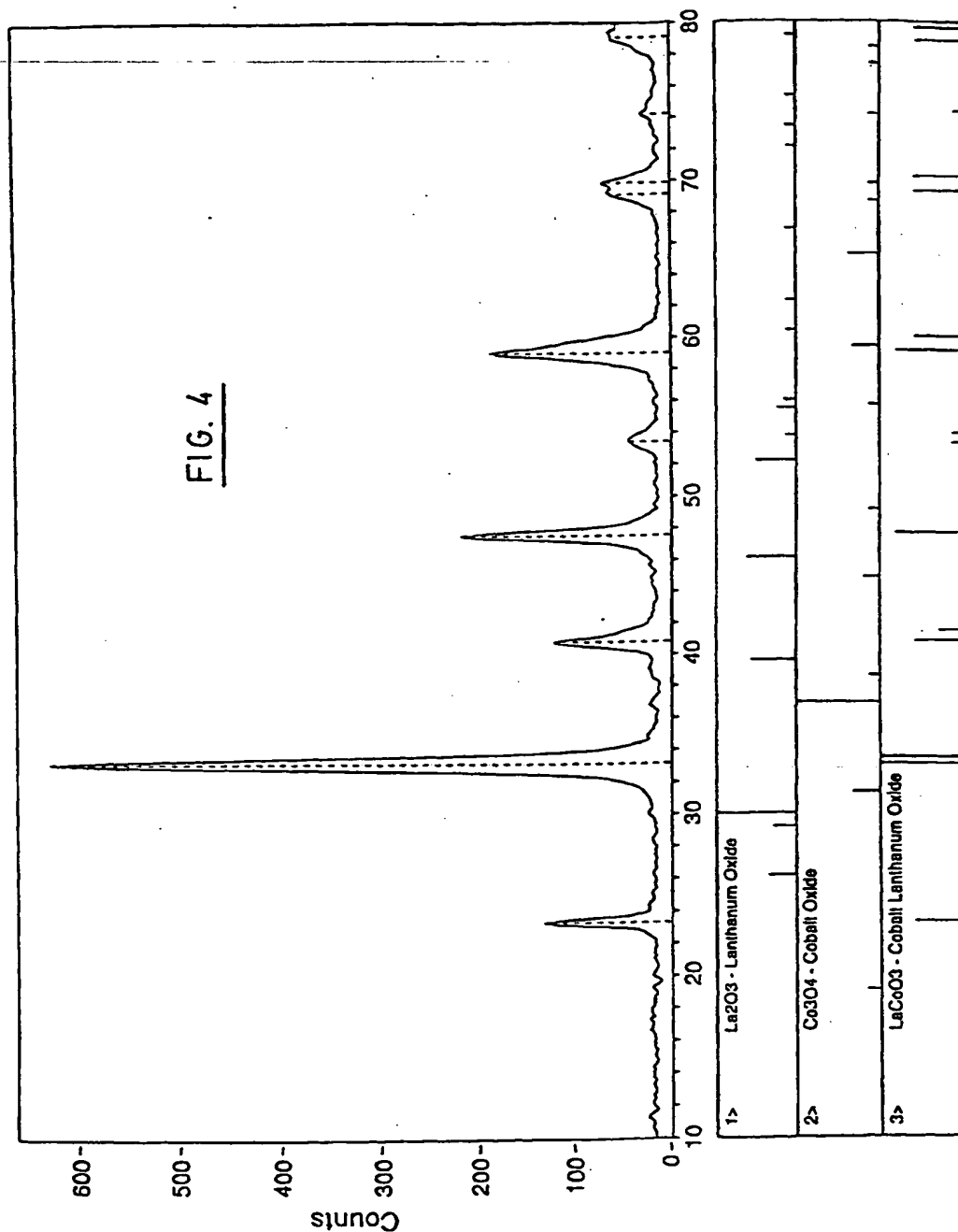


809740-2E29T60





869T20 ZE4ST60



**THIS PAGE BLANK (USPTO)**